HUNGARICA ACTA CHIMICA

AUCTORITATE

ACADEMIAE SCIENTIARUM HUNGARICAE

EDIDIT

CSŰRÖS ZOLTÁN

VOL. I., NO. 3

BUDAPESTINI

MCMXLVIII

THE CATALYTIC DECOMPOSITION OF AMMONIA ON COPPER AND PLATINUM SURFACES.

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SUMMARY.

On the basis of Langmuir's adsorption theory, the usual explanation of the rate law of ammonia decomposition, that is first order reaction with respect to NH_3-concentration and inverse proportionality to H_2-concentration, is as follows: the decomposition is truly monomolecular in the weakly adsorbed NH_3-layer, whereas the H_2 is so strongly adsorbed that it covers practically the whole surface and leaves very little free space for the adsorption of NH_3. This mechanism cannot be the correct one, for two reasons: 1. as a consequence of atomic adsorption the Langmuir adsorption isotherm of H_2 has the form:

$$a = a_\infty \frac{\sqrt{p}}{\sqrt{b} + \sqrt{p}} ,$$

and consequently, following the usual argument, the square root of the H_2-pressure should stand in the denominator of the decomposition rate law, and 2. taking into account the heat of activation of the decomposition — *46* kcal on copper and *44* kcal on platinum surface —, no monomolecular mechanism which could give rise to a first order rate law is possible on energetic grounds. In order to avoid these difficulties it is proposed that the basic picture — according to which the decomposition takes place in the weakly adsorbed NH_3-layer and is retarded by the strongly adsorbed H_2 —, may be retained, but: 1. similarly to the adsorption of H_2 the NH_3 occupies two adjacent places when adsorbed, so that its molecule becomes anchored by two of its H-atoms, the remaining NH-radical pointing away from the surface and 2. the decomposition is the reaction of two such neighbouring radicals forming N_2 and H_2 and leaving four adsorbed H-atoms on the surface. This mechanism seems to be quite satisfactory both from the kinetic and energetic sides.

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The catalytic decomposition of ammonia on copper and platinum surfaces has been the object of many investigations. We may mention the static experiments of *Hinshelwood* and *Burk*,[1] *Schwab* and *Schmidt*,[2] etc. and those of *Dixon*[3] who worked with a flow method. The latter experiments are particularly noteworthy, being free from disturbances which are characteristic about the later stages of the static experiments and so yielding unequivocal reaction orders. According to *Dixon*, even with great excess of H_2, the reaction rate obeys the equation:

$$-\frac{d\,p_{NH_3}}{dt} = k\,\frac{p_{NH_3}}{p_{H_2}},$$

on copper surface at atmospheric pressure between 495 and 620° C, whereas on platinum, between 772 and 858° C, this expression is correct only up to about 100 mm *Hg*-pressure, the retarding effect of H_2 reaching a limiting value at higher pressures, so that the rate of decomposition becomes independent of the H_2-pressure and is only proportional to the NH_3-pressure.

The interpretation of the above rate equation on the basis of *Langmuir's* adsorption theory has become almost banal and is to be found in many textbooks on reaction kinetics. According to this interpretation the decomposition of ammonia is truly monomolecular in the adsorbed layer. The following analysis will prove that this statement cannot be correct and the mechanism is presumably a bimolecular one.

In first instance the monomolecular mechanism is energatically impossible. To show this we start from the following energy values:

a)	energy of one $N-H$ bond in NH_3	90	kcal[4]
b)	bond energy of H_3-molecule	103	„
c)	„ „ „ N_2- „	208	„ [5]
d)	heat of adsorption of H_2 on copper	12	„ [6]
e)	„ „ „ „ H_2 „ platinum	17	„ [7]
f)	„ „ „ „ NH_3 „ „	9	„ [8]

From *d)* and *e)* together with *b)* we have for the heat of adsorption of the H-atoms (this is the state in which H_2 is in fact adsorbed):

g)	heat of adsorption of H on copper	57,5	kcal
h)	„ „ „ „ H „ platinum	60	„

These last two values being almost equal, we may assume with confidence that the heat of adsorption of NH_3 on copper is also practically identical with that on platinum, viz. about 10 kcal. In the decomposition of ammo-

nia, NH_3- and NH-radicals may arise as transitory products, the heats of adsorption of which, in consequence of their increasing insaturation, must be greater. From later considerations we assume about 20 kcal for NH_2 and 30 kcal for NH.

There are four conceivable first steps for a monomolecular decomposition of an adsorbed NH_3-molecule, the heats of reaction of which are, with the above energy values:

$$NH_3\,(Cu) = H\,(Cu) + NH_2 - 42{,}5 \text{ kcal}$$
$$NH_3\,(Cu) = 2H\,(Cu) + NH - 75 \quad ,,$$
$$NH_3\,(Cu) = NH_3\,(Cu) + H - 80 \quad ,,$$
$$NH_3\,(Cu) = NH\,(Cu) + H_2 - 57 \quad ,,$$

As may be seen, all these reactions are highly endothermic. From *Dixon's* experiments the energy of activation of the catalytic decomposition on copper is 46 ± 2 kcal. This value excludes the three latter mechanisms and leaves the first one as the only practicable path, if we assume that its true heat of activation in excess of its endothermicity is only a few kcal. This is not likely but not impossible altogether. If we examine however the further possible ways in which the resulting NH_2-radical may react, we find none which, on energetic grounds, could be much faster than the first step, leaving this as the rate determining one. So the overall reaction could not be of purely first order with respect to the NH_3-pressure. The same considerations are true in connection with the decomposition on platinum, the heats of adsorption being almost identical with those on copper and the heat of activation 44 kcal in the region where the simple rate equation holds true. In the interpretation of their static experiments made at higher pressures however, *Christiansen* and *Knuth*[10] reckon with the last of the four above steps. Since *Schwab* and *Schmidt*[2] found 144 kcal activation energy in this range, this primary reaction cannot be discarded on energetical grounds in this case. There is no doubt however that the mechanism of decomposition is quite different at high and low pressures. In the low pressure range where the rate is purely of first order, the monomolecular mechanism must be discarded.

We may examine now the other factor in the rate equation, the retarding effect of H_2. The inverse proportionality results, according to the current mode of explanation, from strong adsorption of H_2 which covers most of the metal surface. Ammonia can be adsorbed and consequently decomposed only on the portion left free by H_2. If the adsorption can be described by *Langmuir's* isotherm, than with strong adsorption the portion of surface left free is b/p, hence the inverse proportionality. Now we know that the adsorption of H_2 on metal surfaces can not

be described by the simple *Langmuir* isotherm. *Clarke*[9] pointed out that taking the atomic adsorption of hydrogen into account, so that each molecule occupies two adjacent places of the surface, an isotherm results which, identical in form with the original *Langmuir* isotherm, differs from the latter in that it contains the square root of the pressure instead of its first power. *Clarke's* isotherm describes with amazing exactness the adsorption of H_2 and D_2 on copper as measured by *Beebe, Low, Wildner* and *Goldwasser*.[11] According to this isotherm, in the case of strong adsorption, the space left free is inversely proportional to the square root of the H_2-pressure. If the experimentally found retarding effect is however proportional to the first power, this fact points then towards a bimolecular mechanism which would involve two molecules of NH_3 adsorbed on the surface left free by H_2. But in this case the reaction rate should be of second order with respect to the NH_3-pressure provided that the adsorption of the latter gas obeys the simple *Langmuir* isotherm. If we assume however that the NH_3-molecule occupies two adjacent places in its turn on the metal surface, then the adsorption on the first ascending branch of the isotherm is proportional not to the first power but to the square root of the pressure and a bimolecular mechanism results in a first order reaction.

The question arises wether such an adsorption of the NH_3-molecule on two places is both conceivable and probable. We know today that serious catalytic efficiency is barely effected by adsorption of the simple van der *Waals* type. An activated adsorption of the NH_3-molecule on copper and platinum is imaginable only with the intervention of its *H*-atoms, since of the constituents of the molecule the *N*-atoms show no tendency for activated adsorption on these metals (this will not be true with the iron catalysts of ammonia synthesis). The NH_3-molecule is a very flat triangular pyramid. Adsorption on two adjacent places would then mean that the molecule becomes anchored to the surface by two of its *H*-atoms, the remaining *NH*-radical pointing away from it into the gas space. The picture that a triangular molecule may be prone to such a mode of adsorption, is perhaps strengthened by the well known fact that the retarding effect of SO_3 on the catalytic oxidation of SO_2 on platinum is proportional to the square root of its pressure. This is commonly accounted for as an „empirical" exponent, but in the light of the above considerations the explanation obtrudes itself that in this instance too we have to do with an adsorption on two places.

If this picture is true, then in the case of NH_3, the postulated bimolecular decomposition mechanism becomes very impressive: the protruding *NH*-groups of two adjacent adsorbed molecules react with one

another, forming $N_2 + H_2$ and leaving on the surface the four previously anchored H-atoms:

$$2\,NH_3\,(Cu) = 4\,H\,(Cu) + N_2 + H_2.$$

This reaction is endothermic with about 27 kcal on copper and with 17 kcal on platinum. So there remains a true need of activation of some 20—25 kcal which is of the expected order for a reaction of this kind.

The postulated mechanism explaines also the fact that H_2 is seemingly adsorbed much more strongly than NH_3 notwithstanding that their heats of adsorption do not differ greatly. *Dixon* states that the retarding effect of H_2 is proportional to its pressure even when its concentration is not more than one sixth of that of NH_3. Assuming nearly equal rate of adsorption for both gases, this would mean that the rate of desorption of H_2 is less by a factor of about 10^3—10^4. This reasoning of *Dixon* is hardly acceptable, for it means that the desorption of H_2, and only its desorption, has a considerable extra need of activation. If, on the contrary, as we have assumed, the decomposition of NH_3 produces adsorbed H-atoms, this process is equivalent to an ample increase of adsorption rate of H_2 and there is no need for the assumption of a greatly different desorption rate.

For sake of completeness we may return to the statement of *Dixon* that with platinum the retarding effect of H_2 tends towards a limiting value, so that at greater partial pressures the reaction rate becomes seemingly independent of H_2-pressure and is purely of first order with respect to NH_3. Following the argument that the retarding effect increases with the extent of covered area, we are led to the idea that in the limiting range the whole available surface is saturated with H-atoms. As we have assumed above that the adsorption of NH_3 is effected also by H-atoms, it seems improbable that places which are not active for H_2 should be so for NH_3. The NH_3 should then be practically displaced from the surface, so that if decomposition is taking place all the same, we must assume an alternative mechanism. Such a mechanism might involve for instance NH_2-radicals, in two consecutive steps:

1. $NH_3 + H(Pt) = NH_2(Pt) + H_2 - 28$ kcal.
2. $NH_3 + NH_2(Pt) = H(Pt) + N_2 + 2H_2 + 2$ kcal.

The energy values follow on the assumption that the heat of adsorption of the NH_2-radical is about 20 kcal. In this case reaction 2. could be fast enough to leave reaction 1. as the rate determinig step and the heat of activation of 40 kcal found under these conditions is reasonable too. The weak point of this mechanism is obviously the assumption that the counter reaction of 1. is negligible, but there may exist a range of concentrations

where this could be true. At higher concentrations the counter reaction of 1. must manifest itself, and indead, in their static experiments at high pressures *Schwab* and *Schmidt* found the approximate rate equation:

$$-\frac{d\,p_{NH_3}}{dt} = k\,\frac{p_{NH_3}^{1\cdot4}}{p_{H_2}^{2\cdot3}}$$

on platinum, and *Dixon* reports similar results on copper. As shown by *Christiansen*, equations of this kind can be derived on the assumption of preliminary equilibria.

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[11] *Beebe, Low, Wildner* and *Goldwasser*, Journ. Am. Chem. Soc. *57*. 2527 (1935).

DIFFERENCES OF CONCENTRATIONS CAUSED BY DIFFUSION AND THE EFFECT OF GLASS DIAPHRAGMS UPON THE RATE OF DIFFUSION.

BY TIBOR ERDEY-GRÚZ.

(IN COLLABORATION WITH ANDOR HUNYÁR, ÉVA POGÁNY AND ALAJOS VÁLI.)

The knowledge of solvation resp. of hydration in aqueous solutions is of great importance as to estimation of the state of dissolved ions. We lack however any reliable data concerning the number of water molecules in the hydrate sphere of the divers ions ("absolute value of hydration"). Although *Nernst*[1] pointed long ago at the possibilities of solving this problem, it was possible to get data from the hitherto performed investigations only for the so called relative value of hydration ($W = h_k\, n_k - h_a\, n_a$ where h_k resp h_a represents the number of water molecules fixed by a cation resp. an anion [absolute value of hydration] and n_k resp. n_a is the transportation number of the ions). The results concerning the relative values of hydration are however not uniform either. While *Buchböck*[2], *Washburn*[3], *Remy*[4] and others reached trough processes based on measurement of the water transport in connection with electrolysis results agreeing fairly well, *Ulich*[5] achieved considerably lower values from the change of the entropy of ions, from the ionmobility, from anomalies of activity and from electrostriction. It is not surprising that the figures of hydration measured by various methods are not equal, as hydration is not a uniform phenomenon, the water molecules in the hydrate sphere are not fixed by stoichiometric forces and thus the hydrate sphere does not appear at equal rate with various phenomenons. The problem therefore may not be looked upon as totally solved.

As the difference between the hydration of the two ions of an electrolyte may be determined by duly conducted experiments, the

[1] *W. Nernst*, Göttinger Nachr. *1900*, 68.
[2] *G. Buchböck*, Zeitschr. f. phys. Chem. *55*, 584. 1906.
[3] *E. W. Washburn*, Zeitschr. f. phys. Chem. *66*. 549. 1909.
[4] *H. Remy*, Vortschritte der Chem. Bd. *19*. H. 2. 1927.
[5] *H. Ulich*, Zeitschr. f. Elektrochem. —, 497, 1930; Hand u. Jahrbuch p. chem. Phys. Bd. 6. Abschn. II. B. 1.; Zeitschr. f. phys. Chem. A. *168*. 141.

absolute hydration of each ion might be calculated, if the sum of hydration of the ions were also measurable. To this end diffusion experiments seems to be suitable[6], if they are arranged in a way as to contain for comparison an additional substance in equal concentration in the diffusion space and besides to have in one part an electrolyte dissolved. The electrolyte diffusing into the solution — at the beginning free from electrolyte — carries water as a consequence of the hydration of its ions. This transported water changes the concenrtation of the additional substance and if it could be supposed that the latter did not move during the diffusion, the sum of the water transported by the ions could be determined from the change of the concentration of the additional substance. From this sum and from the relative values of hydration (i. e. from the sum and from the difference of the quantity of water transported by the two ions) the absolute numbers of hydration could be calculated. The purpose of our investigations was to ascertain as to how far the diffusion of electrolytes in presence of an additional substance is appropriate for the determination of the absolute hydration of ions and how does the additional substance behave under the circumstances mentioned above.

EXPERIMENTAL PART.

We have performed many experiments for the investigations of the problem mentioned above. Our basic experiments were concerned with the determination of the water resp. of the quantity of additional substance transported by the diffusion of electrolytes. The diffusion was conducted through a glass diaphragm of type *Jena G*4, on both sides of which the additional substance was at the beginning of the experiments of the same concentration and on one side the solution contained besides an electrolyte too. The diffusion through a diaphragm was chosen instead of the free diffusion, because a much exacter result could be attained this way without making the procedure too complicated.

As the results of the experiments differed from those expected on the basis of the relative values of hydration, we have investigated separately whether the glass diaphragms behave as to diffusion in accordance with the size and number of their pores. Therefore we have determined the distribution of different sizes of the pores of various glass diaphragms, the total cross section of the pores and their behaviour as to diffusion and flow of liquids. On the basis of these experiments it could be ascertai-

[6] *W. Nernst*, loco cit.; H. Lotmar, Gött. Nachr. *1900*. 70.

ned that the glass diaphragms generally influence the diffusion of potassium chloride to a measure corresponding to the total cross section of their pores. Thus a special diaphragm-effect does not appear which finding is in accordance with the fact that the average diameter of the pores of the glassdiaphragms *Jena G* 4 used for the experiments is roughly 10,000 times bigger than the molecular dimensions of substances with small molecules.

A) *Experiments concerning transportation of substances. Diffusion apparatus.*

We have used for the study of transport of substances in connection with diffusion the apparatus[7] shown in figure 1. That is essenti-

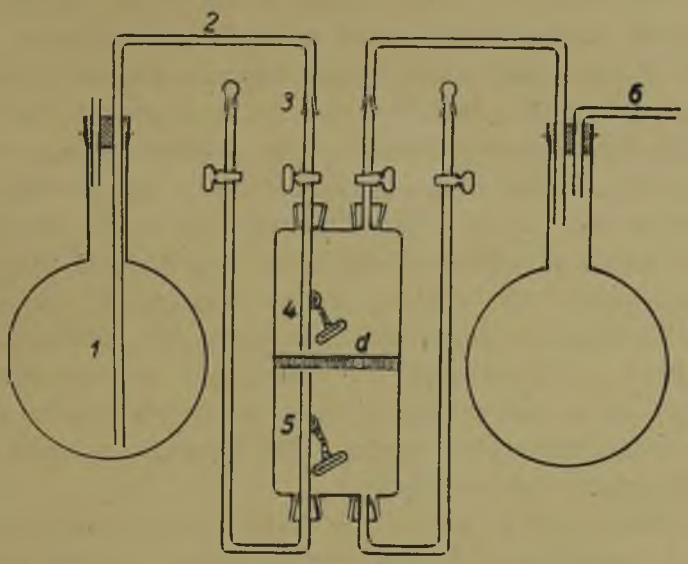

Fig. 1.

ally a cylinder 4 cm in diameter made of *Jena* glass, which is divided into two parts (each of about 70 *ml* volume) by a glass diaphragm of the *Jena G* 4 type (*d.*) The apparatus contains capillary tubes, which are inserted by means of ground glass stoppers as shown in figure. These makes rinsing with boiled water and filling without air bubbles possible. The solution containing the additional substance is filled into the lower part. The solution poured into the upper part contains a solution of the additional substance in the same concentration as the former, and besides an electrolyte too. The latter is diffusing through the glass dia-

[7] *J. W. MacBain* and *T. H. Liu*, Journ. Amer. Soc. *53*, 59. 1931.

phragm into the lower and the purpose of the experiment is to determine the change of the concentration of the additional substance caused by this movement. Thus the upper solution becomes in its lower part more diluted and the lower one in its upper part more concentrated. The mixing effect of the convection caused by that was completed by mixers and thus it was achieved, that the concentration in the lower and the upper part was kept in the course of the experiment uniform. The mixer was an iron rod soldered into a small glass tube, which was fastened to the glasstube (4) resp. (5) by means of a platinum chaine and was kept in perpendicular movement by a magnet outside the apparatus.

The Jena glass diaphragm type Schott *G*4 has pores fine enough (maximum diameter $4-5\mu$) to prevent mixing of the two solutions, on the other hand the pores are large enough to allow for the free diffusion of the dissolved substances of small molecules. In relation to that we have moreover conducted some special experiments too. Some care is needed for preparing the diaphragm for the experiments and for filling the apparatus. First traces of fats must be obliterated in order to make wetting complete. To this end sulfuric acid containing hydrogenperoxyde was the most suitable agent. Secondly care had to be taken, that the concentration gradient corresponding to the beginning of the experiment be established before the start of the experiment. If the experiment started with a diaphragm filled with clean water, the additional substance resp. electrolyte diffusing into the diaphragm and remaining there, would appear as a loss at the analysis of the solutions and would disturbe the evaluation of the results. The apparatus was therefore prepared for the experiment as follows:

After washing with sulfuric acid-hydrogenperoxide mixture the apparatus was rinsed with boiled distilled water, sucked through the diaphragm, until it gave no reaction of sulfuric acid traces. Then the apparatus was filled two-three times with concentrated solution used for the experiment. After one day's stay the apparatus was filled with the experimental solution and allowed to stay for some hours in a thermostat of $25{,}00 \pm 0{,}02^{\circ}$ C. Then followed the final filling respectively the beginning of the experiment.

The solutions for filling the apparatus were previously boiled in vacuum in a beaker (1) and after having taken over the temperature of the thermostat they were sucked by means of tubes (2) and (3) through the apparatus put also into the thermostat by connecting the tube (6) with a waterpump. After having pumped the solution about three times the volume of the upper part of the apparatus, the cocks of the outlet

capillaries of the upper part were closed. The lower part was filled in the same way too. At last the ends of the capillary tubes were closed by means of little ground capsules filled previously with the corresponding solutions and the capsules were also immerged into the thermostat by lowering somewhat the apparatus. Thus it was attained, that in the moment of starting the experiment there was a concentration gradient in the diaphragm corresponding to the difference of the concentrations of the two solutions.

At the end of the experiment the apparatus was lifted as far as to emerge the grinding just above water level, grinding was opened and the solution sucked by means of a dry pipette into a dry beaker and set aside well closed for analysis. Then fresh solution was filled into the apparatus, which was after being closed with its stopper revolved and then the lower part was emptied for the purpose of analysis in the same way.

Choice of substances. The experiments were performed with various electrolytes in the presence of several additional substances, in the choice of which following aspects were kept in mind.

As in course of the experiments only a minute change in the concentration of the additional substance was to be expected, such ones had to be selected, which could be determined wit an accuracy of 0,01%. For eliminating the mutual electrostatic effects between the diffusing ions and the additional substance, it would have been most suitable to use for latter a non-electrolyte. There could however not be found so many non-electrolytes, which were watersoluble, easily determinable in the presence of the electrolytes and fulfilling the other requirements too. Weak acids were therefore also used as additional substances, which though being electrolytes are present mostly in a state of non dissociated molecules. In order to acquire some information about the relation of the transport of substances caused by diffusion to the chemical structure of the additional substance, diverse saturated and unsaturated compounds of different size and containing various numbers of hydroxyl resp. carboxyl groups were chosen. On the basis of these aspects experiments were conducted with following additional substances: arsenic trioxide, propenol, sucrose, acetic, propionic, butiric, laurinic, malic, citric and crotonic acid.

The electrolytes were chosen as to include ions of nearly the same hydration values judged by measurements of their transport numbers, but of different valences, and also ions of different hydration numbers but of the same valence. Table I contains according to *Remy*[8] the

[8] *H. Remy*, Forschr. d. Chemie etc. *19*. 64. 1927; Trans. Faraday Soc. *23*, 385. 1927.

hydration value of ions to be considered, which are calculated from measurements of transport numbers upon the supposition that the absolute hydration value of the hydrogen ion is 1.

TABLE I.

Hydration value of some ions.

$H+$	1,0	$Cl-$	3,0
$Li+$	12,6	$Br-$	2,1
$Na+$	7,4	$J-$	3,7
$K+$	4,1	Acetate	9,4
$Mg++$	14,1		
$Ca++$	12,1		
$Ba++$	4,5		

It is evident from the table, that the salt pairs *KCl* and *LiCl*, further $BaCl_2$ and $MgCl_2$, then *KCl* and $BaCl_2$ and at last *LiCl* and $MgCl_2$ fulfill the requirements mentioned above. Some experiments were besides made with lithium acetate and *KBr* too. It did not seem however worth while to extend our investigations to other anions, because the hydration values of these were not essentially different.

Determination of concentration. The concentration of chlorides, bromides and acids was determined by potentiometric titration, that of arsenic trioxide and propenol by iodometric resp. bromometric method and that of sucrose by the polarimeter. The error with all these methods was kept by proper care below 0,1 per cent of the weighed quantity.

B) *Determination of pore distribution, permeability and cross section of pores.*

In order to clear up the question as to whether the effect of glass diaphragms upon the rate of diffusion corresponds to that expected on the basis of size distribution and total cross section of the pores, these latter data of a great many of diaphragms were determined besides their effect upon the rate of diffusion of potassium chloride solutions and besides their permeability for water flowing through them.

In order to make all these investigations with one and the same diaphragm the rate of diffusion of potassium chloride was determined with a simpler, though less precisely working apparatus. To these experiments filter crucibles of *Jene Glass* were used, through which diffusion was conducted in a way shown in figure 2. The crucible after preparation as described above was put by means of a rubber ring into a glass stoppered broader glass cylinder. The insertion of the crucible was managed as to keep the volumes below and above the diaphragm as far as possible equal. The lower part was filled with boilled distilled

water through the side tube, which might be closed with the ground stopper. The upper part was filled with *KCl* solution and shut by its lid. The apparatus was then put into an air thermostat submerged in a water

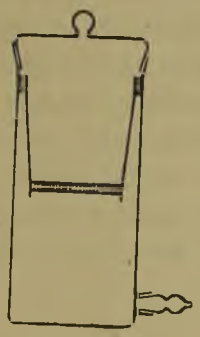

Fig. 2.

thermostat. After diffusion of about two days the liquids of the two parts were poured out, weighed (in order to determine the volume of the two parts) and their concentration determined by potentiometric titration.

On the basis of Fick's 1. law[9]

$$\frac{\log c_0 - \log (c_0 - 2\,c)}{t} = D\,\frac{2q}{2{,}302\,hv} = DK$$

where c_o represents the initial concentration of the solution in the upper part, c the concentration of the solution in the lower part after time t, v the volume of the two parts supposed to be equal,[10] h thickness of diaphragm, q total cross section of pores, D diffusion constant of *KCl*.

In this equation $K = \frac{2\,q}{2{,}302\,hv}$. K is a constant characteristic for the diaphragm (apart from v).

K might thus be looked upon as the measure of quotient q/h, which may be calculated from the determined changes of concentrations and from the known diffusion constant of *KCl*. The size and number of pores in the diaphragm were approximately determined by the method

[9] For the course of calculation see *J. W. MacBain* and *T. H. Liu*, Journ. Amer. Chem. Soc. *55*, 59, 1931; *A. Hunyár*, Dissertation, Budapest, in which the misprint of the deduction published in the former reference is eliminated.

[10] In fact the volumes of the two parts are not equal, that however may be accounted for by simple calculation.

originating from *Erbe*[11] but worked out in detail by *Manegold* and his coworkers.[12]

This is done essentially by exerting an increasing gas pressure upon the diaphragm covered with the liquid. The first bubble passes the diphragm, when the gas pressure exceeds the capillar pressure in the pores of the greatest diameter. As the gaspressure is raised and smaller pores open up, the rate of gasflow through the diaphragm is accordingly increasing. Having thus determined the rate of gasflow through the wet diaphragm as a function of the pressure, the number and diameter of the pores in the diaphragm may be calculated by the method of *Erbe—Manegold*. The calculation is based upon the supposition, that the pores

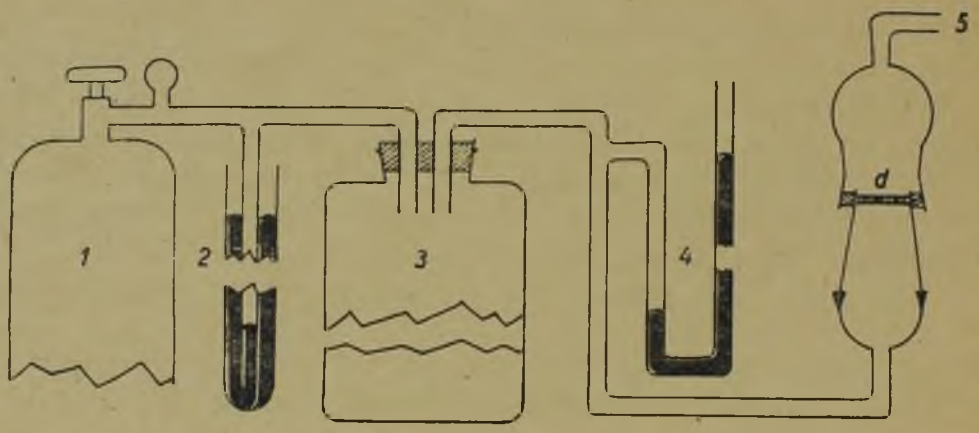

Fig. 3.

are capillary tubes of uniform cross section and their length l is known. This supposition holds of course not strictly for glass diaphragms, because their pores are firstly not cylindrical and secondy their length is not known either. But we may reach approximate results by this method if we substitute a plausible length of pores.

The pore distribution was determined by an apparatus[13] shown in figure 3. The filter crucible containing the glass diaphragm *d* was pressed gastightly between glass connections in the way shown in figure by inserting some rubber rings and an increasing preassure was exerted upon the diaphragm covered with a thin layer of water by means of nitrogen taken from a steel container. The pressure was measured with

[11] *F. Erbe*, Kolloid-Zeitschr. *63*, 277, 1933.

[12] *E. Mangold, K. Solf* and *E. Albrecht*, Kolloid Zeitschr. *91*. 243, 1940; *E. Manegold, S. Komagata* and *E. Albrecht*, Kolloid-Zeitschr. *93*, 166, 1940; *Váli A.*, Dissert. Budapest. 1945.

[13] See *P. Graber* and *S. Nikitine*, Journ. Chim. Phys. *33*, 721, 1936.

the aid of a manometer (4) after inserting a safety valve (2) and a buffer flask (3). The quantity of passing nitrogen was determined by a gas-burett or by a gasmeter. The measurements were taken at 15 ± 1^0 C temperature. Care was taken of the rate of flow not to exceed the value fixed by *Reynold*'s number. Knowing the distribution of the pores, total cross section of the same might be calculated. This however can be controlled by an other way too. It may be proved[14] that the total cross section of the pores:

$$q_p = \frac{l v_p}{d}$$

where v_p represents the total volume of the pores, l the length of the pores supposed to be equal, d the thickness of the diaphragm. The total volume of the pores might be determined by measurement of the weight of water filling the pores.

For the determination of the latter the diaphragms were dried at 110^0 C for three hours, then allowed to cool in a vacuum desiccator and weighed. Then they were freed from air in a vacuum desiccator and still in the vacuum flooded with boiled and cooled water. Thus the pores were filled quantitatively with water. The excess water was blotted from the surface of the diaphragm by means of a *Jena* glass filter with pores just one degree rougher and the diaphragms were weighed. The measurements were reproducible within the margin of 2 per cent.

The permeability of the diaphragm, i. e. the liquid (resp. gas) flow through a diaphragm completely filled with the liquid (resp. gas) under unite pressure is closely connected with the diameter of the pores. The rate of flow of water resp. of nitrogen through the diaphragm was measured in an assembly similar to that shown on figure 3, the diaphragm was however in this case in vertical position. The quantity of liquid passed in a known time under a known pressure was determined in a calibrated vessel.

EXPERIMENTAL RESULTS AND THEIR INTERPRETATION.

A) *Diffusion experiments.*

We have ascertained already through our preliminary experiments that the concentration of additional substances, when present at the diffusion of strong electrolytes, did not change as might have been experted, if the diffusing ions had carried only hydration water, the

[14] *E. Manegold, S. Komagata* and *E. Albrecht*, Kolloid-Zeitschr. 93, 176, 1940.

additional substance however had not been affected. Therefore we tried to clear before all, how the transported quantity depends on the experimental circumstances in the presence of propenol, this being a

TABLE II.

Additional substance: propenol, initial concentration of the diffusing electrolyte: 1 mol/lit.

Diffusing electrolyte	Initial concentration of the propenol mol/lit.	Time of diffusion day	Quantity of propenol in moles transported by one mol of electrolyte
KCl	2	1	0,033
KCl	2	2	0,031
KCl	2	4	0,023
KCl	0,2	2	0,003
KCl	2,0	2	0,031
KCl	5,8	2	0,098
KCl	10,0	2	0,13
KCl	25	2	0,31
LiCl	2,0	2	0,033
$N(CH_3)_4Cl$	2,0	2	0,015
HCl	2,0	2	0,005
KBr	2,0	2	0,025
$LiC_2H_3O_2$	2,0	2	0,041

typical example of additional substances. The results of our experiments referring to this problem are shown in Table II. The first column of the table shows the strong electrolyte used for diffusion, the second column shows the initial concentration of propenol being the same in the whole assembly. The third column shows the time of diffusion, the fourth column contains the quantity of propenol transported by one molecule electrolyte during the experiment expressed in moles as it is received directly by analysis of the solutions. The data given are averages of more parallel measurements. The parallel experiments have resulted in utmost cases figures in agreement within 5% of values given for the transported quantity of the additional substance figuring in the last column. The difference was in no case larger than 10%. The source of these comparatively large errors is, that the quantity of transported additional substance has to be calculated from the small differences of concentrations arising in the course of the experiment, and thus small errors in the determination of concentrations have a comparatively great effect upon the differences.

From tables II and III it is evident, that the concentration of the additional substance increased in that solution, towards which ions of

TABLE III.

Initial concentration of the diffusing electrolytes 1·0 mol/lit, initial concentration of the additional substance 0·27 mol/lit time of diffusion 2 days.

Additional substance \ Diffusing substance	*KCl*	$LiCl_3$	$BaCl_2$	MeC_2
	Quantity (in moles) of the additional substance transported by 1 mol electrolyte			
Propenol	0,024	0,025	0,068	0,061
Acetic acid	0,018	0,037	—	0,083
Propionic acid	0,021	0,041	0,075	0,090
Butyric acid	0,025	0,049	0,085	0,099
Crotonic acid	0,025	0,046	—	0,095
Succinic acid	0,010	0,035	—	0,080
Malicacid	0,010	0,042	—	0,12
Citric acid	0,007	0,042	—	0,10
Sucrose	0,008	0,016	0,025	0,035
Arsenic trioxyd	1,2	—	—	—

the strong electrolyte were diffusing. Thus the ions carry in the course of their diffusion the additional substance to a greater extent, than the hydration water. The only exception is arsenic trioxide, the concentration of which decreased during the diffusion of *KCl* in the solution containing originally none of the strong electrolyte, that means, that the ions of *KCl* have transported thereto more water than arsenic trioxide. But this decrease of concentration is also much smaller, than that which might be expected on the basis of hydration values deducted from measurements of the transport number. The ions of *KCl* transport — no doubt — in the course of their diffusion arsenic trioxide too, the amount of hydration water however overweighs this here.

The results of *Freundlich* and *Krüger*[15] relating to "anomal diffusion" of quinone, according to which a difference of concentration arises in a solution of quinone if potassium sulfate is diffusing in it, are in complete agreement with our findings[16].

As it might occur, that the transport of the additional substance by diffusing ions may perhaps be effected somehow through the presence of the diaphragm, we have conducted some informative experiments under the same circumstances with an *Oeholm* apparatus containing no diaphragm. Though this method is less exact, than the one described above, the free diffusion terminated within the experimental errors in

[15] *H. Freundlich* and *D. Krüger*, Journ. Phys. Chemistry, *43*, 981, 1939.

[16] See our experiments concerning propenol and arsenic trioxide in detail *A. Hunyár*, Dissert. Budapest. 1937.

the same results, thus the diaphragm can not be made responsible for these phenomenons. Table II gives information about the dependence of the transported quantity of the additional substance upon the time of diffusion. The quantity of propenol transported by one mol of *KCl* decreases with increasing time of diffusion. This is explained be the ever growing differences in the concentrations of the additional substance in both parts of the apparatus caused by transportation, which starts rediffusion of the additional substance at an increasing rate. The result of this is, that concentration of the additional substance does not increase with time to such a degree as the quantity of *KCl*, which manifests itself in the virtual decrease of the quantity of the additional substance transported by one mol of the electrolyte as calculated on the basis of the analysis at the end of the experiment. The change of concentration of the additional substance resulting from transport and rediffusion may be calculated [17] also theoretically and the results of calculations are in good agreement with experience. The virtual decrease of the quantity of the additional substance may be thus retraced indeed upon the causes mentioned.

The quantity of propenol transported by one mol of *KCl* is nearly proportional growing with the concentration of the properiol. The diffusing ions thus carry even from the dilutest soluions more propenol, than hydration water. This circumstance is of importance for the evaluation of the phenomenon.

Looking for the cause of the transport of the additional substance, the simplest hypothesis would be, that the diffusing substances carry the molecules of the additional substance fixed as solvates. This would however mean, that solvation is stronger, than hydration even in the dilutest solutions of propenol. If that was (very unlikely) so, an increase of solubility of *KCl* should be expected in the presence of propenol. In order to clear this question, we have measured the solubility of *KCl* at 25° C as a function of the concentration of propenol in the solution.

TABLE IV.

Solubility of KCl in water in presence of propenol.

Concentration of propenol	0	0,5	2,0	4,0	33	volume %
Solubility of *KCl*	31,00	30,01	29,87	28,07	15,78	*g*/100 *ml* solution

The table shows that (as it was excepted) the solubility of *KCl* decreases with the increase of concentration of propenol simultaneously present in the solution. These contradicts to the supposition, that its ions are solvatized stronger with propenol than with water.

[17] *T. Erdey—Grúz* and *A. Hunyár*, Hung. Acta Chimica. *1* 27. 1948.

There is one more fact against the role of solvation and this is, that all of the additional substances enumerated in Table III migrate with ions of the diffusing strong electrolyte. It is hardly conceivable that solvation of these diversely composed substances on all of the ions examined should overweigh hydration.

The transport of the additional substance by diffusing ions seems to be atributable to that kinetic effect, which is exerted upon the (apart from thermical motion) resting molecules of the additional substance by collisions of ions moving in the direction of the decreasing concentration. By means of these collisions a component of preferred direction is added to the random thermical motion of molecules of the additional substance, the result of which is, that these molecules move independently from the concentration gradient and effect a difference of concentrations (this phenomenon must manifest itself also in the change of the rate of diffusion of the non-electrolyte, if ions are diffusing at the same time in the solution).[18] The change of the activity of the additional substance caused by the diffusing electrolyte may however have also its part. In order to clear up these problems further experiments are in progress.

Table III gives information on the behaviour of various additional substances in the presence of divers diffusing ions. In order to make the results comparable, the initial concentrations of the additional substances and that of diffusing electrolytes were the same in all experiments and the diffusion too was of the same duration. Following rules may be roughly deducted from our experimental results:

The various electrolytes carry under the circumstances given the more from the fatty acids examined, the larger the carbon chain of the same is. The different ions carry practically the same amount of butyric acid and crotonic acid, which both contain the same carbon chain and differ only by the olefinic double bond, that means, that as far transportation is concerned double bonds have no considerable effect. Of succinic and malic acid, the latter of which differ from the former by one hydroxyl group, equal quantities are carried by *KCl*, which contains a cation of small hydration value. But in solutions containing the strongly hydrated lithium and magnesium ions, more of the malic acid is transported than of the succinic acid. Thus the hydroxyl group seems to effect transportation only in presence of strongly hydrating cations. *KCl* and $MgCl_2$ transport less, *LiCl* the same amount of the tribasic citric acid as of dibasic malic acid. Transportation of di-and tribasic acids is mostly less than that of monobasic acids if the number of carbon atoms is the same.

[18] See *J. W. MacBain* and *T. H. Sin*, Journ. Amer. Chem. Soc. *53*, 72, 1931.

Bivalent cations transport in every case more of the additional substance, than the univalent cations. The smallest amount transported from among the additional substances examined is that of sucrose; univalent and less hydrated cations carrying less than polyvalent and stronger hydrated ones.

It has been attempted to find a relation between the quantity of transported additional substance and the dipol moment. However such a relation does not seem to exist.

PORE DISTRIBUTION, TOTAL CROSS-SECTION AND PERMEABILITY[19]

In order to clear up the problem as to whether the behaviour of glass diaphragms used for our diffusion experiments may be sufficiently explained simply by the decrease of cross section caused by the presence of the diaphragm, the cross section of many glass diaphragms have been determined by various methods. First of all the number of pores of the different sizes in the diaphragm was determined by the Erbe-Manegold method referred to already (pore distribution). Figure 4 shows the graphs of absolute pore distribution of some Jena glass filters *G* 4 and *G* 3 calculated on the supposition, that the length of pores is the same as the

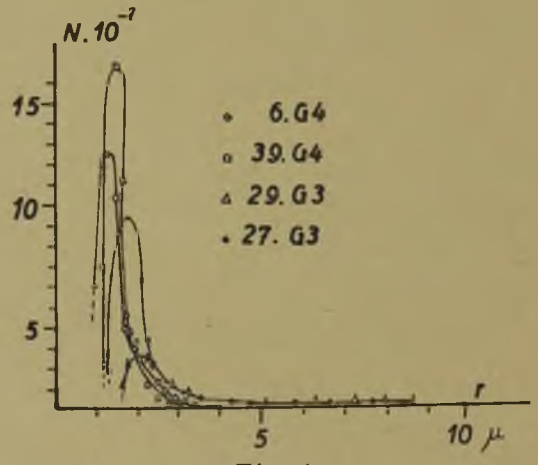

Fig. 4.

height of the diaphragm. This choise being of course arbitrary, is motivated by the equality of the total cross section of pores in both cases either calculated from the distribution of pores or from their volume. In the graphs the radii of pores expressed in mikrons are plotted

[19] For detailed information about measurements and results as to these see *A. Vali* Dissertation, Budapest. 1945.

against the number of pores per cm^2 in the intervall of 0,2 mikron with diaphragms *G* 4 and in the intervall of 0,5 mikron with diaphragms *G* 3 around values of the abscissa. We generally experienced, that the pores of the greatest radii of the diaphragms *G* 4 were of the size of about 4,5—5 mikrons, in the highest number being represented those of the size of 1,2—1,8 mikrons. The corresponding values for diaphragms *G* 3 are 9—10 mikrons resp. 1,8—2,8 mikrons. The graph of distribution is rapidly declining towards the smaller radii, in this direction however no sharp limit can be established. The smallest pore figuring in the graph corresponds only to the highest pressure measurable in the experimental assembly, smaller pores than these (of which there are however but a few) were not opened up at this pressure as yet.

The total cross section of pores may be calculated on hand of the graph of poredistribution. If there are N_i pores supposed to be of circular cross section in one cm^2 area of the intervall i, and the average radius of the pores is r_i, then their cross section in this intervall is

$$q = r_i^2 \pi N_i.$$

The cross section of the total pores in the area of one cm^2 is

$$q = \sum_i q_i$$

On the other hand the total volume of pores under 1 cm^2 area was also determined in the way already described. This is according to those said on page 00. equal to the total cross section of the pores, supposing that the length of pores is the same as the thickness of the diaphragm, table V shows, that values of the cross section calculated in both ways agree fairly well with the diaphragms examined. The existing deviations, which in most cases don't exceed 10 per cent, may be attributed to those simplifying suppositions (cylindric straight pores, the length of which is the same as the thickness of the diaphragm) which had to be introduced in order to avoid disturbing complications in the calculation of the cross section of pores.

From diffusion experiments, which have been performed with diaphragms used for the determination of distribution and cross section of pores, it may be estimated as to how far the change of the rate of diffusion caused by the diaphragms can be attributed to the decrease of cross section. In column 4 of table V the *KD* value is shown as calculated from the diffusion experiments performed with *KCl* in the apparatus described on page 00 (*K* is a constant characteristic for for the diaphragms

according to page 00, D is the the diffusion constant of KCl). If the change of the rate of diffusion depends exclusively on the total cross section, the KD/q quotient must be constant (as K is proportional to q), supposing that the length of the pores in the diaphragm may be taken as equal. According to column 5 of table V this proportion holds to a satisfying measure, if we tak into consideration the uncertainty, which is unavoidably connected with the calculation of q. These experiments resulted thus in the recognition, that the presence of the diaphragm had no other significant influence on diffusion of KCl except the one of diminishing the cross section. This is the same evidently with others substances having not too big molecules.

For further study of the diaphragms their permeability in the sense of page 15. was also determined.

According to the law of Poiseuille[20] is the permeability (a_i) for pore intervall of the sort i is:

$$a_i = \frac{u_i}{p} = \frac{N_i r_i^4 \pi}{8 \eta l}$$

where u_i represents the volume of liquid flown through in 1 second under the pressure p through the openings of poreintervall i and l the length of pores. The total permeability of 1 cm² part of the diaphragm is

$$a = \sum_i a_i = \frac{\pi}{8 \eta l} \sum_i N_i r_i^4$$

The permeability of the diaphragms examined was determined partly by transfusion of water, partly by that of nitrogen (through the dry diaphragm) and the values gained thus directly from the experiments (a_{mess}) were compaired with those calculated on the basis of the graphs of pore-distribution (a_{szk}). The results are summed up in table V. These shows, that the permeabilities measured with nitrogen are higher, than those calculated from pore distribution; the values measured with water are on the other hand smaller. Deviations may be attributed to the fact, that in the case of measurements with nitrogen the diaphragms were quite dry, in case of measurements of pore distribution however they were wet, and thus in this case the water layer on the wall of the pores diminished the cross section. On the other hand the permeability measured with water is smaller, than that calculated from pore distribution, because

[20] See *E. Manegold, S. Komagata* and *E. Albrecht*, Kolloid-Zeitschr. *93*, 176, 1940; *A. Váli*, Dissertation, Budapest. 1945.

in the course of the flow the pores get to some degree stopped,[21] in spite of having used for the flow water, which was formerly filtered through a Jena filter *G* 5. This partial stopping of the pores is manifested also by the decrease of the rate of flow at the beginning of the experiment, the flow becoming permanent only after some 20 minutes. This stopping does not trouble the measurement of pore distribution, because in this case only the very small amount of liquid wetting the diaphragm has to pass the pores. The nature of this stopping however is not yet cleared up sufficiently it may be caused by the swelling of the glass.

The fairly substantial deviations between the permeabilities determined in different ways can hardly be fully explained by stopping, some other factors must apparently be involved there too.

There may be established a very simple relation between the permeability of diaphragms and they effect upon decreasing the rate of diffusion. The constant K characterizing the diaphragm from the viewpoint of diffusion is according to those related on page 13. in following relation to the radiuses of pores

$$(\text{as } q = \sum_i N_i r_i^2 \pi)$$

$$K \,.\, v = s = \frac{2\,\pi}{2{,}302 \,.\, l} \sum N_i r_i^2$$

Compairing this with the expression of a on page 22. the following can be stated concerning the relation of permeability to the behaviour towards diffusion.

$$\frac{a}{s} = h = \frac{2{,}302}{16\,\eta} \frac{\sum_i N_i r_i^4}{\sum N_i r_i^2}$$

The value of h can thus be calculated from the graphs of pore distribution and is comparable with the quotient directly calculated from experimental results. Table V. shows that the deviation of the value h determined by two ways does not exceed 11% with 18, out of the 27 diaphragms examined, and this deviation may be explained by the simplifying suppositions employed in calculation. Nothing can be surly said of the causes of higher deviations appearing at the remaining diaphragms.

[21] *B. F. Ruth,* Inds Engng. Chem. *27,* 708, 806, 1930; *A. Simon* és *W. Neth,* Zeitschr. anorg. allg. Chem. *168,* 221, 1927; *Zakarias,* Koll. Z. *37,* 50, 1925; *Michaelis* and *A. Fujita,* Biochem. Zeitschr. *158,* 11, 28, 1925; *Hüttig* and *W. Neth,* Zeitschr. angen. Chem. *37,* 494. 1924; *G. Tammann,* Zeitschr. anorg. allg. Chem. *158,* 1. 1926.

It seems however on the basis of those said above, that these deviations may be mainly attributed to the errors connected with permeability and thus they do not seem to be in any relation to the rate of diffusion.

TABLE V.

Number of diaphragm	q from pore distribution cm^3	Vol. of pores $(= q)$ cm^3	KD	$\frac{KD}{q}$	a calc. N_2. 10^{-5}	a meas N_2. 10^{-5}	a calc. water 10^{-7}	a meas. water 10^{-7}	s calc. water	s meas. water	h calc. 10^{-8}	h meas. 10^{-8}
1. G4	1,53	1,40	0,1182	0,077	12,1	15,0	21,8	17,5	5,24	4,25	41	41
2. G4	1,40	1,54	0,1243	0,090	9,0	13,8	16,2	16,4	4,63	4,31	34	32
3. G4	1,89	1,88	0,1609	0,085	18,7	23,6	33,4	26,2	7,33	5,80	45	45
6. G4	1,32	1,22	0,1052	0,079	9,4	12,6	16,9	14,6	4,57	3,78	37	38
7. G4	2,22	2,07	0,1936	0,087	29,7	39,2	52,6	43,0	8,33	7,54	63	57
8. G3	1,92	1,69	0,1627	0,084	45,6	76,0	82,2	80,8	0,41	5,46	130	140
15. G4	2,44	2,08	0,1888	0,077	24,8	36,3	50,5	38,0	8,23	7,00	61	54
17. G4	1,94	1,72	0,1408	0,072	15,2	18,6	27,3	20,6	6,29	5,40	43	38
18. G4	2,23	2,20	0,1722	0,077	18,0	23,2	32,2	25,0	7,47	6,28	43	40
20. G4	1,69	1,60	0,1413	0,083	14,6	17,0	26,5	18,2	6,19	5,20	42	36
21. G4	1,61	1,61	0,1380	0,085	9,7	13,8	14,5	16,8	5,23	4,96	33	33
22. G3	1,53	1,63	0,1271	0,083	95,0	127,0	169,8	120,6	4,50	4,20	370	280
24. G3	1,35	1,40	0,1012	0,075	42,6	78,0	76,8	75,3	4,37	3,67	180	200
25. G4	1,91	1,79	0,1568	0,082	16,8	20,4	30,9	24,0	6,37	5,64	44	42
27. G3	1,89	1,73	0,1462	0,077	44,0	89,0	84,2	85,2	6,36	5,26	130	160
28. G4	1,49	1,60	0,1258	0,084	47,0	88,0	84,8	80,3	5,22	4,51	160	170
29. G3	1,97	1,77	0,1430	0,073	61,6	126,0	110,8	105,9	5,45	5,17	200	200
32. G3	1,51	1,71	0,1262	0,083	50,4	74,6	90,8	88,0	3,70	4,52	240	180
33. G3	1,70	1,69	0,1310	0,077	55,2	104,0	99,9	100,0	5,13	4,71	190	210
34. G4	1,50	1,49	0,1102	0,084	9,1	12,7	16,5	14,5	4,51	4,11	36	35
35. G4	1,83	1,76	0,1342	0,073	15,5	19,7	28,0	22,0	5,61	4,94	49	47
36. G4	1,49	1,54	0,1251	0,084	9,0	13,6	16,2	14,1	3,74	4,38	43	32
37. G4	1,86	1,71	0,1522	0,081	14,4	17,8	—	—	7,31	5,65	—	—
38. G4	1,68	1,58	0,1350	0,080	12,1	15,6	21,8	17,1	5,87	5,44	37	31
39. G4	1,81	1,84	0,1556	0,086	14,7	19,2	26,4	18,7	6,68	5,59	39	33
41. G4	1,53	1,66	0,1257	0,082	14,9	20,6	26,8	29,6	5,13	4,51	52	60
G3	1,51	1,47	0,0991	0,075	64,5	106,0	124,4	91,7	3,19	3,24	380	390

The circumstance that the behaviour of diaphragms is determined from the point of view of diffusion by the sum $\sum_i N_i r_i^2$, and from the standpoint of permeability by the sum of $\sum_i N_i r_i^4$, makes it clear that no conclusion can be drawn upon the behaviour as to diffusion resp. permeability from the maximum size of pores (which generally used to be given for characterizing the diaphragms). Thus the total cross section of the pores of some diaphragms containing many pores but of small radii (e. g. Jena filter *G* 4) might by chance be so much the bigger, than that of other diaphragms containing pores less in number but of larger radii (e. g. Jena filter *G* 3), that the rate of diffusion through the diaphragms of small pores becomes greater, than that through the dia-

phragm of large pores. On the other hand the diaphragm of large pores might offer less resistance to the flow, than the diphragm of small pores, thus the rate of filtering is smaller in the case of the latter.

GENERAL CONCLUSIONS.

It may be ascertained on the basis of our experiments, that if in some solution containing a nonelectrolyte or a weak electrolyte in homogeneous concentration the ions of a strong electrolyte are diffusing, the latter carry with them a part of the molecules of the former. This transfer connected with diffusion, which is larger in extent, than the transport of water resulting from hydration, can not be attributed to strong solvation, but it is related to the mechanism of diffusion resp. to the change of activity of the additional substance.

As a consequence of the transport mentioned above diffusion is not appropriate to allow conclusions from the change of concentration of some additional substance upon the amount of hydrate water diffusing together with the ions, at least not until the phenomenons described above are cleared up in every aspect. In connection with that it may be doubtful as to whether ions migrating under the influence of an electric force do not drag with themselves also the additional substance present, even if this did not migrate under the influence of electric forces in absence of ions. (That used to be looked upon as a criterion, whether the additional substance in question is able to be applied as a means for determining relative hydration through measurement of the transport value.) Therefore some doubts arise as to relative hydration values determined through transport numbers and the contradictions among hydration values may perhaps be in relation with the phenomenon mentioned. The investigation of glass diaphragms employed to the experiments are reassuring in that respect, that the rate of diffusion of substances with small molecules is influenced by them only inasmuch as they diminish the cross section.

SUMMARY.

Diffusion of strong electrolytes *(KCl, LiCl, HCl, $N(CH_3)_4Cl$, KBr, $LiC_2H_3O_2$, $BaCl_2$, $MgCl_2$)* was investigated in the presence of additional substances (propenol, sucrose, acetic, propionic, butyric, crotonic, succinic, malic, citric acid and arsenic trioxide), which fill the whole of the solution at the beginning in homogeneous concentration. The diffusion was conducted through a Jena glass diaphragm type *G4* the electrolyte being present at the beginning of the experiment only in the solution on one side of the diaphragm. It was found that the concentration of the

additional substance (with exception of arsenic trioxide) is growing in that part, towards which the ions are diffusing. That means that diffusing ions carry some of the additional substance with themselves. The quantity of additional substance transported is higher, than the amount of water transported in the same time with the hydrate sphere.

The transport of the additional substance is not a consequence of solvation of the strong ions (propenol e. g. does not increase water solubility of *KCl*) but is in some relation — still to be investigated — with the mechanism of diffusion.

The phenomenon described renders diffusion of electrolytes in the presence of additional substances inappropriate for determining hydration values and raises some doubts as to the relative hydration values determined by means of transport numbers.

In order to clear up the part played by diaphragms in the diffusion experiments the pore distribution and total cross section of pores of many Jena glass diaphragms type *G* 4 and *G* 3 were determined besides their influence upon the rate of diffusion of *KCl*. The radius of the largest pores of diaphragms *G* 4 is 4,5—5 mikron (in order to make calculation possible pores are supposed to be cylindric capillaries of the same length). The radius of pores of about 40—50% however is between 1,2—1,8 μ. The radius of the largest pores of diphragms *G* 3 is 9—10 μ; more than half of the pores however have a radius of 1,8—2,8 μ. The influence of diaphragms upon rate of diffusion of *KCl* is proportionate to the total cross section of pores, with such an approximation, which is in accordance to the simplifications applied for calculation. Thus it is to be supposed, that the diaphragms had, apart from the decrease of cross section of the solution, no other observable effect upon our experiments.

The permeability of glass diaphragms for water and nitrogen was also determined. The permeability and the effect of diminishing the rate of diffusion with most diaphragms is in a relation corresponding to their pore distribution. However with some of the diphragms larger deviations appeared also, the cause of which is not yet detected.

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A SPECIAL CASE OF DIFFUSION OF TWO COMPONENTS IN THE SAME SOLUTION.

BY TIBOR ERDEY-GRÚZ AND ANDOR HUNYÁR.

In connection with some other investigations the problem arose as to how the concentration of a substance in solution changes, which fills homogeneously the volume at it's disposal at the beginning of the experiment, if the diffusion of another substance, which has been present in one part of the whole volume only, therein starts and the other substance carries with it the first one in the course of diffusion. As the solution of this problem may be of interest perhaps in some other relation too, details are given below as follows.

Take a vertical vessel of cylindric cross section, which is divided in the middle into two equal parts of volume v by a porous diaphragm (e. g. of glass) of constant characteristics. Both parts be filled with the same solution, which contains substance 1. in the concentration c_1, in the upper part there is besides also an other substance of concentration c_2. Under such circumstances diffusion of the second substance through the diaphragm takes place. Substance 2. is supposed to be carrying by some reason with it to some esctent substance 1. too, on account of which the concentration of the latter changes in the two parts of the apparatus. As a consequence of the resulting difference of concentrations diffusion of substance 1. also begins and the substance transported from the upper space into the lower one rediffuses into the upper space. The pores of the diaphragm be large enough to make the free diffusion of substance 1. and 2. (being both of small molecules) possible and causing no membran effects, but again small enough to prevent mixing of the two solutions. Let the concentrations of both, lower and upper part be separately homogeneous during the whole process.

The problem is to calculate as to how the quantity of substance 1. passed through the diaphragm changes during the diffusion as a function of time, the change being attributed partly to transportation by substance 2., partly to rediffusion. Let us first calculate how the quantity of substance 2. diffused from the upper part into the lower one depends upon time. If dm_2 represents the quantity diffused in time dt,

D_2 the diffusion constant of substance 2., q the cross section through which diffusion takes place, h the thickness of the diaphragm, Δc_2 the difference of concentrations on the two sides of the diaphragm, then according to Fick's law

$$\frac{dm_2}{dt} = D_2 q \frac{\Delta c_2}{h} \tag{1}$$

the change of concentration in the diaphragm supposed to be homogeneous.

To calculate Δc_2 it must be taken into consideration, that at $t = 0$ $\Delta c_2 = c_2$ (then none of substance 2. is present in the lower part), and in time t after the start of diffusion

$$\Delta c_2 = c_2 - \frac{2 m_2}{v} \tag{2}$$

if m_2 represents the quantity of substance diffused from the upper part into the lower one in the course of time t. (The concentration namely decreased by m_2/v in the upper part and increased by the same amount in the lower one.) Thus (1) may be expressed

$$\frac{dm_2}{dt} = \frac{D_2 q c_2}{h} - \frac{2 D_2 q}{hv} m_2 = \frac{1}{2} A v c_2 - A m_2 \tag{3}$$

where

$$A = \frac{2 D_2 q}{hv}$$

After differentiating equation (3)

$$\frac{d^2 m_2}{dt^2} + A \frac{dm_2}{dt} = 0 \tag{4}$$

One supposed solution of these linear differential equation be then

$$m_2 = e^{rt}$$

$$\frac{dm_2}{dt} = r e^{rt} \text{ , and } \frac{d^2 m_2}{dt^2} = r^2 e^{rt} \tag{5}$$

Substituting these values into equation (4) we have the characteristic equation of the differential equation:

$$r^2 + Ar = 0 \tag{6}$$

The two radicals of this are

$$r_1 = 0 \text{ and } r_2 = -4.$$

Thus the general solution of the differential equation is

$$m_2 = k_1 + k_2 e^{-At} \tag{7}$$

The values of the constants K_1 and K_2 may be calculated from the conditions:

if $t = 0$, then $m_2 = 0$ that is $0 = k_1 + k_2$ respectively $k_2 = -k_1$ thus

$$m_2 = k_1 (1 - e^{-At}) \tag{8}$$

If again $t = \infty$ the concentrations have become balanced and the concentration of both parts become equal to the half of the concentration of the upper part:

in the case of $$t = \infty, \; m_2 = \frac{c_2 v}{2}$$

thus on the basis of (8)

$$k_1 = \frac{c_2 v}{2}$$

Substituting this value into equation (8)

$$m_2 = \frac{c_2 v}{2}(1 - e^{-At}) = \frac{c_2 v}{2}(1 - e^{-2 D_2 qt/hv}) \tag{9}$$

This is the quantity of substance 2. which diffused through the diaphragm in t time.

Now we may proceed to the investigation of the diffusion of substance 1. This one fills the solutions on both sides of the diaphragm in equal concentration at the beginning of the diffusion. The change of it's concentration is caused by substance 2. each molecule of which carrying f molecules of substance 1. during the diffusion. If m_2 of substance 2. diffuses in t time through the diaphragm, the transported quantity of substance 1. is

$$m_1' = f m_2 \tag{10}$$

and at the same time

$$dm_1' = f dm_2 = f D_2 q \frac{\Delta c_2}{h} dt = \frac{f D_2 q c_2}{h} dt - \frac{2 f D_2 q}{hv} m_2 dt \tag{11}$$

Due to transportation the concentration of substance 1. changes also on both sides of the diaphragm and as a result of the difference of concentrations brought about thus, it's diffusion in the opposite direction i. e. from the lower part to the upper one begins. Fick's law holds of course also

for the quantity of substance 1. diffusing in time dt

$$dm_1'' = D_1 q \frac{\Delta c_1}{h} dt = \frac{2 D_1 q m_1}{hv} dt \tag{12}$$

The quantity (m_1) of substance 1. apparently passed through the diaphragm is after all composed partly of the quantity (m_1') transported downwards by substance 2. from above and partly of the quantity (m_1'') transported through diffusion initiated in the opposite direction:

and

$$\begin{aligned} m_1 &= m_1' - m_1'' \\ dm_1 &= dm'_1 - dm_1'' \end{aligned} \tag{13}$$

substituting (11) and (12) into (13)

$$dm_1 = \left[\frac{f q D_2 c_2}{h} - \frac{f 2 q D_2}{hv} m_2 - \frac{2 D_1 q}{hv} m_1\right] dt \tag{14}$$

or introducing the following notation

$$A = \frac{2 D_2 q}{hv} \quad \text{and} \quad B = \frac{2 D_1 q}{hv}$$

$$\frac{dm_1}{dt} = \frac{1}{2} f A v c_2 - f A m_2 - B m_1 \tag{15}$$

Differentiating this equation

$$\frac{d^2 m_1}{dt^2} + f A \frac{dm_2}{dt} + B \frac{dm_1}{dt} = 0 \tag{16}$$

The value of dm_2/dt may be calculated after differentiating equation (9)

$$\frac{dm_2}{dt} = \frac{c_2 v}{2} A e^{-At} \tag{17}$$

Substituting this value into equation (16) the differential equation of the diffusion of substance 1. is reached

$$\frac{d^2 m_1}{dt_2} + B \frac{dm_1}{dt} = - \frac{A^2 c_2 f v}{2} e^{-At} \tag{18}$$

In order to solve this secondary inhomogeneous linear differential equation let us introduce following abbreviations

$$b = - \frac{A^2 c_2 f v}{2} \tag{19}$$

$$\frac{d^2 m_1}{dt^2} + B \frac{dm_1}{dt} = b e^{-At} \tag{20}$$

Differentiating this equation and dividing by $-A$

$$-\frac{1}{A}\cdot\frac{d^3 m_1}{dt^3}-\frac{B}{A}\cdot\frac{d^2 m_1}{dt^2}=be^{-At} \tag{21}$$

Substracting equation (21) from equation (22)

$$\frac{d^3 m_1}{dt^3}+(A+B)\frac{d^2 m_1}{dt^2}+AB\frac{dm_1}{dt}=0 \tag{22}$$

Thus we reached a linear homogeneous differential equation of 3. order. Taking as one of the supposed solutions of this

$$m_1=e^{rt} \tag{23}$$

then $$\frac{dm_1}{dt}=re^{rt},\ \frac{d^2 m_1}{dt^2}=r^2 e^{rt},\ \frac{d^3 m_1}{dt^3}=r^3 e^{rt}$$

Substituting these values into equation (24)

$$r^3+(A+B)r^2+ABr=0 \tag{24}$$

The radicals of this are $r_1=0$, $r_2=-A$, $r_3=-B$ and the general solution of the differential equation is

$$m_1=k_1+k_2 e^{-At}+k_3{}^{-Bt} \tag{25}$$

In order to determine the constants k_1, k_2 and k_3 let us differentiate the latter equation twice

$$\frac{dm_1}{dt}=-k_2 Ae^{-At}-k_3 Be^{-Bt}$$

$$\frac{d^2 m_1}{dt^2}=k_2 A^2 e^{-At}+k_3 B^2 e^{-Bt}$$

Substituting these values into equation (20) and simplifying

$$k_2 A^2-k_2 AB=b$$

from this

$$k_2=\frac{b}{A(A-B)} \tag{26}$$

The values of k_1 and k_3 may be calculated from the limiting conditions: in time $t=0$ $m_1=0$ (none of substance 1. has diffused as yet), thus on the basis of (25)

$$k_1+k_2+k_3=0 \tag{27}$$

Again after infinite time the concentrations of substanace 1. and 2. become equal in the entire space i. e. in the case of $t=\infty$ $m_1=0$ (the

entire quantity of substance 1. passed from the upper part into the lower one got back again into the upper one). Thus from equation (25) $k_1 = 0$ and $k_3 = -k_2$ substituting the values of k_1, k_2 and k_3 into equation (25)

$$m_1 = \frac{b}{A(A-B)} (e^{-At} - e^{-bt}) \qquad (28)$$

Resubstituting the values of A, B and b the quantity of substance 1. passed after all through the diaphragm in time t is received:

$$m_1 = \frac{f D_2 c_2 v}{2(D_2 - D_1)} (e^{-2 D_1 qt/hv} - e^{-2 D_2 qt/hv}) \qquad (29)$$

The solution of the problem purposed in the introductory lines was controlled also experimentally. For that reason one part of a diffusion-apparatus described elsewhere[1] was filled with a normal solution of potassium chloride ("substance 2") containing 5 per cent propenol ("substance 1"). The other part being separated from the first one by a glass diaphragm was filled with a solution of 5 per cent propenol. The quantity of potassium chloride and propenol passed after all through the diaphragm in 1, 2 respestively 4 days was determined. The quotient of these two quantites m_1/m_2 is decreasing with time. Most of substance 1 (propenol) is carried namely by substance 2 (*KCl*) in the first moment of diffusion, because by this time rediffusion of substance 1 did not begin as yet. With time increasing rediffusion is growing in scope (supposing that the total balance of concentrations be far enough) and thus the quantity of substance 1 apparently transported by one molecule of substance 2 is decreasing by and by. After extrapolation of the value m_1/m_2 to time $t = 0$ f received, i. e. the quantity of substance 1 really transported by one molecula of substance 2. From the experiments mentioned above $f = 0{,}036$.

Table below contains the values received experimentally for the molecules of propenol apparently transported by one molecule of potassium chloride (m_1/m_2) (column 2) and those calculated on the basis of equation (9) and (29) (column 3). Following data were used for the calculations

D_{KCl}	= 1,66 cm²/ day	v	= 0,0683 lit
$D_{propenol}$	= 0,95 „ „	f	= 0,036
q/h	= 0,0071 cm	c_2	= 1,0 mol/lit.

[1] *Tibor Erdey-Grúz*, Hung. Acta Chimica *1.* 7. 1948.

TABLE.

Quantity of propenol apparently transported during diffusion by one molecule of potassium chloride (m_1/m_2).

Duration of diffusion	m_1/m_2 measured	m_1/m_2 calculated $D_{propenol}$	m_1/m_2 calculated $D_{propenol}$
1 day	0,034	0,032	0,033
2 ,,	0,031	0,029	0,030
4 ,,	0,024	0,022	0,025

It is evident from the table, that the values theoretically calculated and experimentally measured in the case examined as an example agree fairly well. The deviations may be attributed besides the experimental errors very likely to the change of diffusion constants used as a basis for calculation, the constants being derived from experiments with solutions containing the substance in question alone. These constants may however change if there is also an other substance present in the solution. To that points also, that if the value of the diffusion constant of propenol $D = 0{,}76$ is substituted for that measured directly ($D = 0{,}95$), the calculated and experimentally found values agree better. As to the influence of the diffusion constants of various substances upon each other further investigations are planned.

SUMMARY.

Following special case of diffusion was investigated. A solution placed into two cylindric spaces of the same volume and separated by a diaphragm contains in both parts a substance in equal concentration, in one part there is also an other substance present. This latter diffuses through the diaphragm into the other space and carries with it a part of the other substance too. Thus the concentration of the first substance becomes different in the two spaces and the rediffusion of the substance begins in the opposite direction. We have calculated how the quantity of the substance passed (apparently) after all through the diaphragm (quantity transported by the second substance—rediffused quantity) is related to time. The quantity of substance 1 apparently transported by one molecule of substance 2 is the largest at the beginning of diffusion, then it gradually decreases on account of the rediffusion. The calculated and experimantally found values agree fairly well, the deviations may be attributed very likely to the change of diffusion constants substances in the presence of other substances.

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A CONTRIBUTION TO THE THEORY OF MIXED CRYSTALS

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(RECEIVED: 12. V. 1946.)

It is well-known that crystals precipitated from the mixture of solutions of certain isomorphous substances contain both of these without showing the least signs of inhomogenity on macroscopic or *X*-ray examination. According to our present views ions of identical sign can substitute each other if their radii are not very different. In this way a crystal lattice is formed whose lattice constants and eventually angles are at a slight variance with the respective data of the pure constituents. Usually a difference of 15% or more in the lattice constants of the pure componets makes the mixed crystal formation impossible, but in most cases there is considerably less difference between the lattice constants of the pure substances crystallizing together.

Apart from the fact that we can not prepare perfectly pure elements or compounds so that they are always mixed crystals, such are produced often purposely e. g. a great many industrial alloys. The problem of the structure of mixed crystals is therefore very important not only from theoretical point of view but also in practice. An exact treatment was, however, as far as we know, not made yet, the possibilities being tested only in a qualitative way.

A mixed crystal could have three conceivable structures, i. e. 1. the vicariating ions are placed perfectly at random; 2. it is constituted of very minute, parallel crystallites of the pure constituents; or 3. the different ions are placed in a regular way. *X*-ray diagrams give the possibility of testing these instances, with the result that case 2. can not be realized since then the diagrams of both pure substances should appear which does not occur. On the other hand case 3. would involve extra reflexions besides the original reflexions of the pure compounds, although experiment gives no evidence of such (more exactly, such extra reflexions show the formation of a so-called superlattice which occurs only in certain alloys within a short composition range, but was not meet with in ionic crystals). Only case 1. remains therefore as the single possibility. We shall deal below only with ionic lattices.

Relying on experimental evidence we must conclude that no deviation can exist in the lattice constant of elementary cells of the mixed crystal containing different ions, since otherwise it would not be possible to build up a regular body from them. As the charge density of ions is decreasing exponentially outwards from the nucleus and the equilibrium distance is also influenced by thermal agitation, the possibility of a uniform lattice constant in the mixed crystal is given although small domains have much differing composition. In agreement with *Vegard's* empiric rule the lattice constant can be interpolated linearly from the respective lattice constants of the pure constituents, corresponding to the composition. It is probable that a strain arises between the parts of different composition but as far as this is not too big, the mixed crystal can be maintained.

Our purpose is to determine the results following from the statistical structure of the mixed crystal, first of all its lattice constant and lattice energy. An adequate theory should also account for the possibility of mixed crystal formation between certain isomorphic substance pairs, since it is known that not all of them are capable to form mixed crystals (e. g. $CaCO_3$ and $NaNO_3$). We are discussing alkali halogenide crystals of type B 1 (rock-salt) with the semi-empirical method of *Born* and *Mayer* (1). This is specially suited to numerical calculations since it can be accomplished much more quickly than other methods of deeper foundation, so it is perfectly sufficient for a first orientation.

The forces holding together an ionic lattice are mainly of electrostatic character; besides the *Coulomb* attracting force a repulsion exits which prevents ions of opposite sign from approaching beyond a certain limit. The repulsion term contains two constants which may be determined from the empirical molecular volume and compressibility. We must considerer two more energy terms although small but important from the point of view of the stability. One of them, the *Van der Waals* term is inversely proportional to the sixth power of the distance; *London* has shown that it is in connection with the polarizability of ions and arises — in a first approximation — from the perturbance of the zero-point energy of the oscillator consisting of two ions. The other corresponds to the kinetic zero-point energy appearing in the *Fermi* statistical theory. The expression of lattice energy as used after *Born* and *Mayer* is therefore

$$E = -A(r) + B(r) - \frac{C}{r^6} + \varepsilon_o$$

It is an experimental fact, that from the mixture of the solutions of isomorphic substances mixed crystals precipitate on evaporating;

the lattice energy of these crystals must be therefore less than that of a mixture of pure crystals of identical composition. We made our calculations on an elementary octahedron with a cation in its centre and different anions on its apices; all possible arrangements have been considered.

Our calculations involve the molecular volume and the compressibility of the mixed crystal. As for the first, it changes in a linear way between the molecular volumes of the pure crystals, as shown e. g. by *Retgers*. Owing to the lack of experimental data we supposed the same behaviour for the compressibilities, which is, of course, admissible only *faute de mieux*.

The lattice constant was determined on the hand of the variation principle assuming that the state with the lowest lattice energy is most stabile.

The polarizability of ions and the polarization energy arising from it which is of the same sign as the *Coulomb* and *Van der Waals* term, is usually not considered, although it contributes considerably to the stability. This is justifiable because it falls out in the first order by symmetry and on the other hand the constants of the repulsion term are so determined as to embrace this effect. In mixed crystals, however, the symmetry is lost in most of the elementary octahedrons, since the opposite anions are not always the same and in consequence they polarize the central cation differently, even the electron clouds of negative ions are dislocated somewhat from their symmetrical arrangement.

According to electrodynamics the polarization energy is

$$E = \frac{1}{2} \alpha \mathfrak{E}^2$$

where α is the polarizability of the ion and $\mathfrak{E}$ the field intensity. In this form the polarization energy of pure crystals vanishes in first approximation and its higher terms are included in the repulsion energy. In rock-salt type mixed crystals the polarization energy does not vanish at all, its value being

$$E_{p1} = \frac{1}{2} \alpha \left\{ \sum_{i=1}^{6} \mathfrak{E}_{oi} \right\}^2 \text{ where } | \mathfrak{E}_{oi} | = e \left[\frac{1}{r^2} - \frac{1}{(r + \Delta r)^2} \right]$$

where Δr denotes the difference of radii of the opposite anions.

The other polarization term follows from the fact that the electron clouds of ions are somewhat deformed within the limits of tolerance. In all probability the electron clouds of anions surrounding the central

cation are arranged so that the electron density changes identically between them, i. e. the nucleus of anion remains on the apex of octahedron whilst the electron cloud is flattened in the direction of the bigger anion and extended against the smaller one. If we would regard the ions as rigid spheres we could say they are placed in a way that their distances be the same. But owing to the said dislocation the field intensities deriving from the opposite ions can not neutralize each other even in the case of identical ions being opposite. We can do the calculations in a first approximation by considering the apparent dislocation of ions as a real one.

We calculated in this way the lattice energy for all pairs of alkali halogenides with rock-salt structure (*NaCl—NaBr, KCl—KBr* etc.), moreover the lattice constant corresponding to the minimal lattice energy for mixed crystals of those compositions for which the cation is surrounded by 0, 1, 2 . . . 6 anions of one and 6, 5 . . . 1, 0 anions of the other kind.

Our results are tabulated for *NaCl—NaBr* mixed crystals in Table I. Here r is the lattice constant, m the number of Br^- ions on the octahedron apices, $A(r)$ tle *Coulomb* and $B(r)$ the repulsion term, c/r^6 the *Van der Waals*, ε_0 the zero-point energy and E_{p1} resp. E_{p2} the polarization terms. If 2, 3 or 4 ions of the other kind are on the apices, a symmetrical and an asymmetrical arrangement is possible; in Table 1. the upper value corresponds to the symmetrical and the lower row to the asymmetrical one. E_0 is the lattice energy without polarization and E the whole lattice energy; E_{lin} is the energy calculated from the pure crystals by linear interpolation.

Comparing our results with those of *Born* and *Mayer* resp. *Mayer* and *Helmholz* (2) as seen in Table II (naturally for pure *NaCl* and *NaBr* only, which they calculated), some difference is perceptible.

The difference is only a slight one in the lattice constant (0,03—0,5%) and somewhat more in the lattice energy. It arises from two grounds, first the new value of electron charge determined since that time (being about ½% larger); secondly, we did not suppose the coefficient ϱ occurring in the repulsion term be constant as the authors mentioned above did, but calculated it from the aforesaid equations, so our result can be taken as more reliable.

As seen from Table I, the lattice energy of the mixed crystal calculated by us is less than the sum of lattice energies of the pure components taken in appropriate proportion, but the difference does not exceed 0,007% even in the most favourable case. An effect of this order of magnitude could not be detected experimentally. Although the sign of the effect calculated is right, its magnitude is too small; but we have

TABLE I.

Lattice constants and lattice energies of NaCl—NaBr mixed crystals.
(For particulars see text.)

m	r . 10^{-8} cm	$A\ (r)$	$B\ (r)$	c/r^6	ε_0	E_{p1}	E_{p2}	E_o	E	E_{lin}	$E_{lin}-E_o$	$E_{lin}-E$
		10^{12} erg/molecule										
0	2,7971	−14,4100	1,5311	−0,2075	0,1200	—	—	−12,8664	−12,9664	−12,9664	—	—
1	2,8259	−14,2632	1,5042	−0,2078	0,1167	−0,0006	−0,0009	−12,8501	−12,8516	−12,8471	0,0030	0,0045
2	2,8552	−14,1167	1,4795	−0,2069	0,1133	— −0,0008	— −0,0021	−12,7308	−12,7308 −12,7337	−12,7279	0,0029	0,0029 0,0058
3	2,8852	−13,9700	1,4524	−0,2048	0,1100	−0,0005 −0,0010	−0,0008 −0,0023	−2,6124	−12,6137 −12,6157	−12,6087	0,0037	0,0050 0,0070
4	2,9158	−13,8233	1,4248	−0,2026	0,1067	— −0,0008	— −0,0008	−12,4944	−12,4944 −12,4960	−12,4894	0,0050	0,0050 0,0066
5	2,9471	−13,6766	1,3991	−0,1995	0,1033	−0,0005	−0,0006	−2,3737	−12,3748	−12,3703	0,0034	0,0045
6	2,9791	−13,5300	1,3735	−0,1945	0,1000	—	—	−12,2510	−12,2510	−12,2510	—	—

TABLE II.

Lattice constants and lattice energies of NaCl and NaBr, after Born and Mayer (upper row) and the present authors (lower row).

	r. 10^8 *cm*	Difference %	E in 10^{12} erg/mole	Difference %
NaCl	2,812	0,5	12,63	2,66
	2,7971		12,9664	
NaBr	2,978	0,03	12,05	1,67
	2,9791		12,2510	

got effects of similar sign and magnitude for such pairs of alkali halides, which do not give mixed crystals. It is evident from these results that the compressibilities of mixed crystals can not be as great as calculated by linear interpolation.

On the other hand we got the remarkable result that the lattice constant calculated without special assumption is in perfect agreement with the experimental values (and the rule of *Vegard* (3) corresponding to a linear interpolation). Although the compressibilities used by us for mixed crystals can not be correct, their influence in the calculation of lattice constants is much less than in the case of the lattice energy. It is interesting to note that the compressibilities of alloys are mostly bigger than those of the pure constituent metals. The experimental determination of compressibilities of mixed crystals is therefore an interesting problem, which we hope to attack.

We mention the fact too, that restricting ourselves to the four energy terms of *Born* and *Mayer* we get the maximal deviation from the linear value if 2 (or 4) different ions are present in the octahedron. If the polarization terms are taken into account, the asymmetric configurations turn out more stable, as expected for the statistic case. Further polarization terms may be considered, but their effect will be in any case less than the error in the calculated compressibilities.

Budapest, Institute of Physical Chemistry of the Palatin Joseph University of Technical Science, May 1946.

SUMMARY.

By using the *Born—Mayer* expression the lattice energy and lattice constant of *NaCl—NaBr* mixed crystals was calculated. Only two constants, the molecular volume and the compressibility of the mixed crystals are necessary; the latter was computed by linear interpolation from the compressibilities of the pure crystals. In this way we have got the correct values of the lattice constants of the mixed crystals (in agreement with the *Vegard* rule). The calculated lattice energy of the mixed crystal is

lower than that of the pure salts but the difference is too small. This is due to the assumption as regards the compressibility, which therefore can not be interpolated but must be determined experimentally.

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(1) *M. Born* and *J. Mayer*, Zeitschr. f. Phys. **75** (1932) 1.
(2) *J. Mayer* and *L. Helmholz*, Z. f. Phys. **75** (1932) 19.
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SEPARATION OF COPPER FROM CADMIUM BY THIOSULFATE.

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(RECEIVED 10. II. 1946. PRESENTED BYE SCHULEK, MEMBER OF THE ACADEMY.)

Copper is forming with thiosulfate a colourless complex anion of the composition $Cu_2(S_2O_3)_2$, which after acidifying and boiling of the solution decomposes forming a heavy black precipitate of copper I sulfide. The processes of this quantitative precipitation of copper are as follows:

$$2\ CuSO_4 + 2\ Na_2S_2O_3 = Cu_2SO_4 + Na_2SO_4 + Na_2S_4O_6$$

(reduction of copper)

$$Cu_2SO_4 + 2\ Na_2S_2O_3 = Na_2\,(Cu_2(S_2O_3)_2) + Na_2SO_4$$

(formation of complex)

$$Na_2\,(Cu_2(S_2O_3)_2) = Cu_2S + S + SO_2 + Na_2SO_4$$

(decomposition of complex).

If the solution contains also cadmium, this remains in solution and can be determined in the filtrate. The method of separation was first suggested by *G. Vortman*[1]. According to the findings of the author however larger quantities of copper and cadmium can not be separated completely in one operation. Copper I sulfide always contains a considerable amount of cadmium, thus a second precipitation is unavoidable. Though the precipitate is purer if the solution was more acidified, it is however never free of cadmium. The cadmium content of copper I sulfide precipitated only once may be proved in the simplest way by converting the sulfide into oxide by heating and precipitating the copper electrolytically from the solution of the oxide smelt after disclosing it with pyrosulfate. In the electrolyte thus freed of copper the presence of cadmium may be proved by means of hydrogen sulfide.

The procedure leading to the results related below is as follows: 100 *ml* of the solution of copper and cadmium weakly acidified with sul-

[1] Z. analyt. Chem. 20, 416 (1881) and *A. Orlowsky*, Z. analyt. Chem. 21, 215 (1882).

furic acid is mixed in a beaker of 400—500 *ml* with a solution of 10—20 per cent sodium thiosulfate until it becomes colourless, and then acidified with 12 *ml* sulfuric acid 1 : 1. The solution is heated under frequent stirring till boiling, is then covered with a watchglass and boiled vigoronsly for about 15 minutes more,until the supernatant becomes quite clear. After some minutes it is filtered through a Schleicher—Schüll filter: No 589[I] and the precipitate washed a few times with hot water. The precipitation, filtering and washing does not take more than half an hour. The precipitate is put with the filter into a quarz crucible and heated to convert the sulfide into oxide. The oxide containing some cadmium is disclosed with potassium pyrosulfate ten times it's quantity, which procedure lasts but a few minutes. After having rinsed the particles of the cooled smelt from the lid into the crucible with some hot water the smelt is covered with hot water and the crucible is put on a waterbath. After one hour and a half the smelt has become as loose as to be rinceable from the crucible. (If applying a used crucible some silicic acid residue may get into the solution, which must be filtered off. The copper is precipitated after complete solution of the smelt in the way described above for a second time, the Copper I sulfide thus freed from Cadmium is converted into oxide by heating and measured as copper oxide. See "remarks" below.)

The joined filtrates contain the cadmium. In the course of further proceedings however much sulfur is precipitated from the polithyonic acids in the solution. This is for the determination of cadmium inconvenient.

Sulfur may be eliminated very easily from the solution with the author's procedure as follows.

The solution of 250—300 *ml* is entirely evaporated in a *Jena* glass dish on a waterbath. The dish covered with a watchglass is heated on an asbestos wire net with a small flame until the remaining sulfuric acid just begins to boil. Then 10 *ml* water is poured into the somewhat cooled dish through it's effluent, the watchglass is rinsed and the liquid is stirred. The sulfur became meanwhile roughly crystalline, although the solution is from some colloidal sulfur still turbid. In order to oxidize the colloidal sulfur, the glass dish is put on a waterbath and after the liquid took it's temperature 8—10 *ml* saturated bromine-water solution is added at once under stirring. The small amount of colloidal sulfur is oxidized immediately. After having removed the superfluous bromine on a waterbath in about a quarter of an hour the roughly crystalline sulfur is filtered off and rinsed with hot water several times. The filtered liquid thus reached at is always quite clear. Cadmium is determined as *CdS* or

$CdNH_4PO_4 . H_2O$. If cadmium is to be determined as sulfide, the solution is diluted as to contain not essentially more than 0,02 *g* cadmium and 3 *ml* concentrated sulfuric acid for every 100 *ml* solution. (There are 12 *ml* of concentrated sulfuric acid already in the solution resulting from the double precipitation of copper.) Hydrogen sulfide is passed into the solution heated previously to boiling temperature until its complete cooling. The reddish precipitate is collected in a *Jena* filter crucible 1 *G* 4 and washed with cold water. The precipitate is dried on 100 C° and measured as *CdS*.

If cadmium is to be determined as $CdNH_4PO_4 . H_2O$, the metal is precipitated first as sulfide and after dissolving the filtered sulfide the precipitation of phosphate is proceeded to. The direct precipitation as cadmium ammonium phosphate from the strongly acidic and with ammonia neutralized solution would not be appropriate on account of the presence of the large quantity of ammonium sulfate. The solution which amounts to about 400 *ml*, is heated to boiling, and then saturated with hydrogensulfide till cooling off. The resulting precipitate is collected on a filterpaper (*Schleicher—Schüll* 595) and washed with cold water. The sulfide is dissolved on the filter with hot diluted hydrochloric acid 1 : 1 and the filter is rinsed with hot water. The solution of cadmium is evaporated to dryness. The precipitation of phosphate is effected as follows. Diammoniumphosphate (solved in 20 *ml* water) amounting 15 times the quantity of cadmium is added to the neutral or very slightly acidic solution which amounts 100 *ml* and is stirred up. The precipitate is collected next day in a filtercrucible of the *Jena* 1 *G* 4 type using for rinsing water saturated with cadmiumammonium phosphate. The precipitate is rinsed then three times with 5 *ml* cold water each time, then twice with 5—5 *ml* concentrated ethanol and at last three times with 5 *ml* ethylether each time. The precipitate is dried at 100° C and weighed as $CdNH_4PO_4 . H_2O$.

Smaller quantities of cadmium (0,01 *g* and less) are precipitated from a solution of 25—30 *ml*.[2] Rinsing is done accordingly with less water, ethanol and ether.

The results of separation of larger quantities of copper and cadmium are shown in Table I.

If the quantity of metals to be separated is less — up to 0,05 *g* copper and cadmium — the copper I sulfide precipitates free of cadmium. Thus separation is effected in one process. In this case cadmium is determined most suitably as *CdS*. The filtrate of copper is after elimination

[2] If Cadmium in 100 *ml* amounts to 0,01 *g*, the precipitate is crystallized only after two days stay.

TABLE I.

Separation of larger amounts of copper and cadmium with sodiumthiosulfate. The separation can not be effected in one process. The copper I sulfide containing cadmium was converted into Copper II oxide by heating, the oxide was rendered solvable by $K_2S_2O_7$ and the precipitation was repeated. Determination of copper: as CuO, that of cadmium partly as CdS and partly as $CdNH_4PO_4 . H_2O$.

Calculated Cu g	Found Cu g	Difference mg	Calculated Cd g	Found Cd g	Difference mg
0,1037	0,1039	+ 0,2	0,1037	—	—
0,0980	0,0978	— 0,2	0,0897	0,0896	— 0,1
0,0890	0,0982	+ 0,2	0,2108	0,2109	+ 0,1
0,0980	0,0978	— 0,2	0,2106	—	—
0,0980	0,0977	— 0,3	0,2102	0,2100	— 0,2
0,0492	0,0492	± 0,0	0,2090	0,2088	— 0,2
0,0980	0,0976	— 0,4	0,0383	0,0381	— 0,2
0,1037	0,1041	+ 0,4	0,0901	0,0903	+ 0,2

of the sulfur diluted to 200—250 *ml* and precipitation is effected as above. Results as to that are shown in Table II.

TABLE II.

Separation of small amounts of copper and cadmium with sodium thiosulfate. Determination of copper as CuO; determination of cadmium as CdS. Separation succeeds in one process.

Calculated Cu g	Found Cu g	Difference mg	Calculated Cd g	Found Cd g	Difference mg
0,0103	0,0101	— 0,2	0,0105	0,0103	— 0,2
0,0103	0,0105	+ 0,2	0,0105	0,0100	— 0,5
0,0205	0,0204	— 0,1	0,0210	0,0212	+ 0,2
0,0411	0,0411	± 0,0	0,0418	0,0421	+ 0,3
0,0411	0,0413	+ 0,2	0,0418	0,0416	— 0,2
0,0514	0,0513	— 0,1	0,0523	0,0527	+ 0,4
0,0514	0,0518	+ 0,4	0,0523	0,0525	+ 0,2

The single separation gives good results also in the case of extreme quantitative proportions. (See Table III.)

Remarks to the determination of copper as CuO and to that of cadmium as $CdNH_4PO_4 . H_2O$.

Copper precipitated as sulfide may be determined in the simplest way as CuO. According to general opinion this procedure is reliable only with small amounts. The author's own experience shows however, that both Cu_2S and CuS can be converted by heating into pure copper II oxide (CuO) if the amount of copper does not exceed essentially 0,15 g. A strong Teclu burner is sufficient for heating. The precipitate should not contain after heating reddish parts (Cu_2O, Cu). In such a case the crucible is heated in slanted position for about ten minutes with a strong

TABLE III.

Separation of copper and cadmium with sodiumthiosulfate in extreme quantitative proportions.

Determination of copper as *CuO*; determination of cadmium as *CdS*.

Separation succeeds in one process.

Calculated *Cu* *g*	Found *Cu* *g*	Difference *mg*	Present *Cd* *g*
0,0103	0,0102	— 0,1	0,20
0,0103	0,0104	+ 0,1	0,20
0,0103	0,0105	+ 0,2	0,20
Calculated *Cd* *g*	Found *Cd* *g*	Difference *mg*	Present *CU* *g*
0,0105	0,0107	+ 0,2	0,20
0,0105	0,0105	± 0,0	0,20
0,0105	0,0106	+ 0,1	0,20

TABLE IV.

Found *Cu* *g*	Calculated *Cu* *g*	Difference *mg*
Precipitation as Cu_2S Determination as *CuO*		
0,1306	0,1284	+ 0,1
0,1473	0,1284	+ 0,1
0,1260	0,1284	— 0,3
Precipitation as Cu_2S Determination as *CuO*		
0,1307	0,1285	+ 0,1
0,1474	0,1289	+ 0,5
0,1257	0,1285	+ 0,1

TABLE V.

Determination of cadmium as $CdNH_4PO_4 \cdot H_2O$ in pure solutions of cadmium acetate.

Calculated *Cd* *g*	Found *g*	Difference *mg*
0,1685	0,1682	— 0,3
0,1803	0,1801	— 0,2
0,1878	0,1877	— 0,1
0,1461	0,1463	+ 0,2
0,2128	0,2125	— 0,3
0,2127	0,2124	— 0,3
0,1038	0,1034	— 0,4
0,0929	0,0929	± 0,0
0,0973	0,0971	— 0,2
0,0966	0,0963	— 0,3
0,0938	0,0935	— 0,3
0,0505	0,0501	— 0,4
0,0416	0,0413	— 0,3
0,0108	0,0107	— 0,1

Teclu flame, after which the oxide becomes homogeneously black. The use of an electric furnace is very advisable. The reliability of this procedure is proved by data in Table IV.

Cadmiumammonium phosphate can be dried at 100 C⁰ without loss of crystall water. The presence of ammoniumsalts do not interfere with the results at all. These statements originate from *Lewis W. Winkler*[3] and the experiments of the author confirm them. (Table V and VI) 3 *g* of sodiumsulfate in 100 *ml* solution don't interfere either (Table VII).

TABLE VI.

Determination of cadmium in presence of ammoniumsalts as $CdNH_4PO_4.H_2O$.

g $(NH_4)_2SO_4$ in 100 *ml* solution	Calculated *Cd* *g*	Found *Cd* *g*	Difference *mg*
5	0,1170	0,1167	— 0,3
7	0,1710	0,1707	— 0,3
7	0,1328	0,1325	— 0,3
g NH_4NO_3 In 100 *ml* solution			
7	0,1020	0,1025	+ 0,5
7	0,1020	0,1025	+ 0,5
g NH_4Cl In 100 *ml* solution			
7	0,1020	0,1023	+ 0,3
7	0,1020	0,1020	± 0,0

TABLE VII.

Determination of cadmium in presence of sodiumsulfate as $CdNH_4PO_4 . H_2O$.

g Na_2SO_4 in 100 *ml* solution	Calculated *Cd* *g*	Found *Cd* *g*	Difference *mg*
3	0,1134	0,1131	— 0,3
3	0,1935	0,1937	+ 0,2
3	0,2100	0,2104	+ 0,4

[3] Z. angew. Chem. 34,466. (1921).

A szerkesztésért Csürös Zoltán, a kiadásért Voinovich Géza felelős.

49.098. — Egyetemi Nyomda, Budapest. (F.: Tirai Richárd.)

The HUNGARICA ACTA CHIMICA are being published by the *Hungarian Academy of Sciences* in Budapest, edited by Prof. Zoltán Csűrös (Budapest).

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